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(54) Hydrocarbon processing

(57) A process for the catalytic conversion of synthesis-gas into a product which comprises naphtha, kerosine and distillate is characterized in that the catalyst is a Fischer-Tropsch catalyst also containing a zeolite, the naphtha fraction contains 60% or less linear paraffins and the kerosine and distillate fractions contain more linear paraffins and olefins than found in the naphtha fraction. Reduction of the relative amount of straight chain material in the naphtha fraction increases the octane number and so enhances the quality of the gasoline product, while the high quality of the kerosine and distillate fractions is maintained.

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HYDROCARBON PROCESSING

5 Background of the Invention

This invention relates to improvements to the Fischer-Tropsch process for the conversion of synthesis-gas into hydrocarbons.

The Fischer-Tropsch process is a well known and 10 researched process for the conversion of mixtures of carbon monoxide and hydrogen, known as synthesis-gas, into hydrocarbons. The process is described in "Fischer-Tropsch and Related Synthesis" by H. Storch, N. Golumbic and R.B. Anderson, John Wiley and Sons 1951. A

more recent review of Fischer-Tropsch is given by M.E. Dry in "Catalysis Science and Technology" (J.R. Anderson and M. Boudart (eds.)) Vol. 1, Springer Verlag 1981.

In essence the Fischer-Tropsch synthesis takes place over the metals iron, cobalt, nickel or ruthenium, supported or unsupported, containing promoters or additives which enhance activity or suppress unwanted byproduct formation.

In the particular instance of the invention, a component of the Fischer-Tropsch catalyst is a zeolite. Zeolites are crystalline alumino-silicates which are described in "Zeolite Molecular Sieves" by D.W. Breck, John Wiley & Sons 1974.

The liquid products of the FT process may conveniently be described as a four component mixture comprising naphtha (b.p. C₅ to 195°C), kerosine (b.p. 195 to 235°C) and distillate (b.p. 235 to 315°C), and fuel oil (b.p. > 315°C).

The presence of a high proportion of linear hydrocarbons is desirable in the kerosine and distillate fractions, which confer on the product a high cetane number and a low octane number. On the other hand the quality of the naphtha fraction is enhanced by the presence of branched and unsaturated hydrocarbons and aromatics which result in a higher octane number.

The major product of the classical FT process is linear paraffins, and consequently the quality of the naphtha fraction is unsatisfactory. Previous attempts to enhance the quality of the naphtha fraction by restructuring have resulted in concomitant undesirable restructuring of the kerosine and distillate fractions.

Process of the Invention

It is an object of the present invention to provide a modified FT process which results in a preferential restructuring of the naphtha fraction, 5 compared with a minor restructuring of the kerosine and distillate fractions.

Consequently there is an improvement in quality of the naphtha without substantial deterioration in the quality of the kerosine and distillate fractions.

10 In one aspect the invention provides a process for conversion of synthesis-gas into a product which comprises three components, naphtha (b.p. C₅ to 195°C), kerosine (b.p. 195 to 235°C) and distillate (b.p. 235 to 315°C) in which the naphtha fraction is modified to 15 contain branched alkanes and alkenes. More particularly, the modified naphtha fraction contains not more than 60% linear paraffins, while the kerosine and distillate fractions contain more linear paraffins and olefins than are present in the naphtha fraction.

20 Synthesis-gas is a general term used for a gas comprising substantial portions of carbon monoxide and hydrogen. The gas may also contain carbon dioxide and water. Synthesis-gas can be made from any carbonaceous source, by the known processes of partial oxidation, 25 gasification or steam reforming. The relative concentrations of the gaseous components depends upon the source of the synthesis-gas and the process chosen. Sources for synthesis-gas include coal, oil shale, petroleum hydrocarbons and natural-gas.

30 In the process of the invention, no limits are placed on the composition of the synthesis gas however the composition will to some extent reflect the choice of source. For example, coal derived synthesis-gas is characterized by a relatively high carbon monoxide 35 content (ratio of hydrogen to carbon monoxide being typically ca 0.5 mole/mole), whereas for natural gas

derived synthesis-gas the hydrogen content is somewhat higher (ratio of hydrogen to carbon monoxide being typically ca. 2 or more).

The ratio of hydrogen to carbon monoxide is 5 also influenced by the technology chosen to produce the synthesis-gas. For instance steam reforming of natural-gas gives a hydrogen to carbon monoxide ratio of 10 3 or more whereas partial oxidation of the natural-gas gives a ratio of 1.5 or less. Once produced the ratio of 15 hydrogen to carbon monoxide can be adjusted to any value by separation or the use of the water-gas shift reaction.

We have been particularly interested in 20 natural-gas derived synthesis-gas as a means of utilizing Australia's abundant natural-gas reserves, however the 15 process of the invention is not limited to the high hydrogen content synthesis-gas usually derived from natural-gas by steam reforming.

The Fischer-Tropsch synthesis converts 25 synthesis-gas into hydrocarbons ranging in weight from methane to heavy waxes. The distribution of the hydrocarbons produced is in accordance with the Schulz-Flory distribution whereby the ratio (in mole terms) of material of any given carbon number bears a simple relationship to the material at the next highest 20 carbon number, this ratio being the Schulz-Flory Alpha value (α).

$$\frac{\phi_{(n+1)}}{\phi_n} = \alpha$$

30 wherein ϕ_n and $\phi_{(n+1)}$ are respectively the number of moles in carbon numbers n and $n + 1$, and α is a constant less than unity. The Schulz-Flory Alpha Value is a known

method of describing the product distribution in Fischer-Tropsch synthesis, see for example U.S. Patent 4,595,703.

Now if alpha is ca. 0.6, substantially all the 5 hydrocarbon product produced (90%) will boil at less than 195°C i.e. be naphtha or light gases. If alpha is greater than ca. 0.95 most of the product will be heavy wax b.p. higher than 315°C. The process of the invention relates to Fischer-Tropsch processes giving substantial 10 amounts of hydrocarbon boiling in the naphtha (C₅-195°C), kerosine (195 to 235°C) and distillate (235 to 315°C) ranges, and will thus apply to Fischer-Tropsch synthesis with alpha values in the range 0.6 to 0.95 and more 15 preferably to 0.65 to 0.85, when the product contains significant quantities of kerosine and distillate and is not heavily laden with heavy-wax.

Classical Fischer-Tropsch catalysts comprise an active metal (iron, cobalt, nickel or ruthenium) which may be supported (for example on alumina or silica) and 20 promoted with small amounts of other materials; for example iron catalysts are usually promoted with small quantities of potassium, and cobalt catalysts can be promoted with thoria. Many compositions of Fischer-Tropsch catalysts are described in the 25 literature. The principal products of Fischer-Tropsch synthesis are normal paraffins and olefins.

Zeolites constitute one component of the Fischer-Tropsch catalyst pertinent to this invention. Zeolite catalysts are well known in performing 30 shape-selective hydrocarbon transformations. Zeolites have been described as components of Fischer-Tropsch catalysts where they are said to bring about shape-selectivity to the synthesis. In the prior art, the use of zeolites to influence the product distribution 35 has been directed towards maximising the naphtha fraction at the expense of the kerosine and higher fractions.

For example, Dwyer and Garwood in U.S. Patent 4,463,101 describe the use of an iron Fischer-Tropsch catalyst in association with a high silica zeolite for the conversion of synthesis-gas into olefinic naphtha.

5 This patent, like many others, utilises zeolites of the ZSM-5 family. The ZSM-5 zeolite, with a ten-ring port, has been found particularly useful in limiting the synthesis product to the naphtha fraction and there are many examples of its use for this purpose.

10 Other zeolites can also be used, for example smaller port zeolites such as erionite or larger port zeolites such as faujasites.

Zeolites are more fully described by D.W. Breck in "Zeolite Molecular Sieves" (Wiley 1974). Zeolites are 15 crystalline open pored structures with openings in the range of molecular dimensions, which can allow the entry and egress of simple molecules such as those found in transport fuels to the interior of the crystal. Zeolites are principally alumino-silicates but other elements can 20 substitute for the aluminium or silicon. Such elements include gallium, germanium and phosphorus. Some of these substituted materials are known by names other than zeolites e.g. SALPOS which comprise open pored structures of alumina, silica and phosphate. The term zeolite is 25 used here to include all such open structures which can permit the entry and egress of molecules of the size found in transport fuels.

The Fischer-Tropsch synthesis can be performed over a range of pressures, a wide range of space 30 velocities and over a wide temperature range. By comparison to the influence of temperature, space velocity and pressure only slightly influence the product distribution. At low temperatures heavier materials are favoured and as temperature is raised lighter material is 35 formed. In other words increasing temperature lowers the alpha value. When combined with zeolites,

Fischer-Tropsch catalysts tend to be operated at relatively high temperatures ($>250^{\circ}\text{C}$), typically 280°C or 300°C . Under these conditions, the alpha value is naturally low, independent of any shape selective action of the zeolite.

The process of this invention requires that the alpha value be preferably not less than ca. 0.65. This places an upper limit on the temperature of operation at about 270°C .

10 In order for the zeolite to be effective, the temperature of the system will be required to be above some limit typically ca. 220°C . Operation below this limit, depending upon and probably peculiar to the particular catalyst, may produce essentially 15 Fischer-Tropsch products as if the zeolite component were absent; that is, not show branching selectivity as the carbon number changes.

The process of the invention, in temperature terms, is preferably carried out in the range 220 to 20 270°C , at GHSV and pressures optimum for the particular catalysts, for example under the following conditions:

Temperatures:	220 to 270°C
Pressure:	0.1 MPa to 5 MPa, preferably 1 to 4 MPa
25 GHSV:	50 to 10,000, preferably 100 to 5000
Alpha:	0.60 to 0.95, preferably 0.65 to 0.85

Of these parameters, the value of alpha is more important than the temperature.

The zeolite component of the Fischer-Tropsch catalyst brings to the catalyst an acidic function, which is placed in a restricted environment. Without being bound by any theory, in order to be restructured, the normal paraffins and olefins produced by the Fischer-Tropsch component of the catalyst will need to

diffuse through the zeolite to the active centres within the zeolite crystals. This means there will be a diffusion limitation to the conversion of the unbranched hydrocarbons.

5 Restructuring for the linear paraffins and olefins proceeds to produce an increase in the amount of branching in the chain. At higher severities, further restructuring to aromatics and other cyclic species may occur. The requirement is that the amount of linear 10 product is significantly reduced in the naphtha fraction but restructuring will be less for the higher boiling fractions.

The choice of zeolite is an important aspect of the invention. Without wishing to be limited by any 15 theoretical considerations, we believe that the required action is one of chain length selectivity whereby lighter (b.p. to 195°C) paraffinic and olefinic hydrocarbons are able to diffuse to the active centres within the zeolite crystal more rapidly than are heavier (b.p. over 195°C) 20 paraffins and olefins. Such selectivity we intuitively expect not to be abrupt (although abrupt chain length selectivity has been observed in the cracking of normal paraffins over erionite), but a gradual change over the boiling range of the Fischer-Tropsch product. 25 Nevertheless, the point to be realised is that the lighter products (naphtha) diffuse more rapidly and are hence more reactive than the heavier products (kerosine and higher fractions).

Thus, the first principle in the selection of 30 the zeolite component is that normal paraffins and olefins can readily diffuse into the crystal. Upon reaching the active centre, the paraffins and olefins will be skeletally isomerized or further processed to branched aliphatics. These molecules must be able to get 35 out of the zeolite which defines the lower limit of pore size to be those corresponding to 10-ring windows.

The zeolite must also be capable of carrying an acid function and be stable under the condition of the FT synthesis.

Examples of zeolites fulfilling these 5 requirements are ZSM-5, and ZSM-11, Zeolite Y and dealuminised Zeolite Y. It would be expected that many other zeolite structures such as ZSM-12, mordenite, dealuminised mordenite and Zeolites X and L would be effective. This list is not meant to be limiting in any 10 way.

The optimisation of the relative quantities of the various components of the catalyst of the invention, Fischer-Tropsch metal (or metals), promoters, supports, zeolite, and binder and the optimisation of the 15 performance of the catalyst is easily performed by one skilled in the art.

The preferred Fischer-Tropsch metal is cobalt. One example of a catalyst employed according to the invention will contain 5 to 50% cobalt and 10 to 90% 20 zeolite, any balance being made up by promoters, inert supports and/or catalyst binders.

An important aspect of this invention is the consideration of the value of the Fischer-Tropsch products as hydrocarbon fuels or blends.

25 In classical Fischer-Tropsch, molecules with straight carbon-chains are the principal components, monomethyl isomers being present in small amounts. Such a product leads to good quality distillate and kerosine fractions which in consequence are of high value. 30 Unfortunately, this is not the case with the naphtha fraction where straight molecules lead to product of low octane number (typically ca. 40). Using zeolites in the catalyst, at high temperatures (ca. 280°C) gives a naphtha of improved octane value (e.g. 80 or more), but 35 little or no kerosine or distillate fraction is formed.

Fischer-Tropsch product is a broad boiling range material and thus can be said to resemble crude oil. Crude oils are subject to variation in quality, for instance due to sulphur content. In the case of 5 Fischer-Tropsch product there is no sulphur present which leads them to be ranked with the better crude oils.

Another important quality differential is based on the reduction in the relative amount of straight chain material in the naphtha cut, which increases the octane 10 number and so enhances the quality of the gasoline product. The products of the invention have branched paraffins and olefins present in the naphtha fraction. The result is that a high quality naphtha is formed.

However, in the kerosine and distillate 15 fractions, the absence or low amounts of branched chain material is considered important because if present in these fractions they lead to a lower cetane number. The products of the invention have comparatively low amounts of branched chain material in the kerosine and distillate 20 fractions. Thus the high quality of Fischer-Tropsch kerosine and distillate is maintained.

Fuel-oil (b.p. over 315°) is one of the least useful fractions of crude oil and substantial quantities have to be cracked into gasoline, especially in countries 25 like Australia with a high gasoline and low fuel-oil demand. The products of the invention are low in fuel-oil fraction, leading to the whole product being easily processed by conventional oil refineries.

The product of the invention is thus a premium 30 quality synthetic crude oil.

The following examples illustrate the process of the invention. In all of the examples, the feed is synthesis gas with a v/v ratio of CO:H₂ of 1:2.

Example 1

This illustrates the synthesis of a simple Fischer-Tropsch catalyst (code FT18).

The zeolite, H-ZSM-5 (4.43g, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 40$) was impregnated with cobalt nitrate solution (2.44 g in 2.5 ml water). The catalyst was dried overnight at 90°C . The catalyst was formed into extrusions with the aid of acid washed bentonite (2/1, w/w, catalyst/bentonite), then fired at 500°C .

10 By mercury intrusion porosimetry the surface area was measured to be $16.2 \text{ m}^2/\text{g}$ with a pore volume of 0.47 cc/g.

Analysis showed the catalyst contained Co_3O_4 , 9.6%; Al_2O_3 , 9.8%; Fe_2O_3 , 1.3%; SiO_2 , 72%; H_2O , 6.0%.

15 Before use, the catalyst was broken and sieved to size fraction 1-2mm.

Example 2

The catalyst (1.2 ml) of Example 1 was charged into a microreactor. The catalyst was pretreated at 20 350°C in hydrogen (100ml. min.^{-1} at 0.1 MPa) for 16hr.

The catalyst was cooled to a reaction temperature (280°C). After synthesis the catalyst was reactivated in hydrogen at 350° before synthesis at 220°C and then again before synthesis at 250°C . All syntheses were performed 25 at $\text{GHSV} = 1000 \text{ hr}^{-1}$ at 2MPa with a synthesis-gas ratio of 1.88/l, v/v, H_2/CO .

The results of the synthesis are given in Table 1.

TABLE 1

Run	FO22/3	FO23/3	FO21/3
Temperature	220	250	280
5 (deg. C)			
Time on Line (hr)	195	96	93
CO Conversion % (Average)	8	36	71
10 Alpha Value	0.82	0.74	0.58
<u>n-paraffin</u>			
Other products			
at:-			
C10	2.21	1.73	0.95
15 C13	1.82	1.97	0.92
C17	2.12	2.13	1.58

The run at 220°C shows little selectivity in the product as witnessed by the ratio of n-paraffins to 20 other products at carbon numbers 10, 13 and 17. The conversion in this instance is also very low at 8%.

The run at 280°C produces a product very rich in naphtha (alpha value less than 0.6) and little selectivity is observed in the product.

25 At 250°C, the process of the invention is illustrated. The alpha value at 0.74 shows the product will contain reasonable quantities of kerosine and

distillate, obtained at reasonable conversion (36%). Further as the weight of product increases so does the amount of n-paraffin in the product.

Examples 3 to 6

5 These examples illustrate the invention, and were carried out under the following conditions:

temperature 240°C; pressure 2MPa; GHSV 1000

Catalyst	Conversion	CO	n-Alkane proportions		
		(%)	α	C_9-C_{11}	$C_{11}-C_{13}$
3. 100 Co:500 ZSM-5(95)	88	0.84	0.36	0.42	0.49
4. 100 Co:1000 ZSM-5(95)	65	0.81	0.27	0.32	0.46
5. 100 Co:500 ZSM-5(95):500 SiO_2					
15 6. 100 Co:18 ThO_2 :1000 ZSM-5(95)	67	0.85	0.51	0.57	0.67
	66	0.79	0.27	0.33	0.55

Example 7

20 This example shows that a critical temperature is required to effect selectivity. Conditions are the same as examples 3 to 6 with the exception that the temperature is 230°C instead of 240°C.

Catalyst	Conversion	CO	n-Alkane proportions			
		(%)	α	C_9-C_{11}	$C_{11}-C_{13}$	$C_{13}-C_{18}$
as Example 3		70	0.79	0.52	0.51	0.60

Examples 8 to 12

These examples show the benefits of zeolites (8, 9 and 10) compared with other supports (11 and 12) in the process of the invention.

5 These examples were carried out under the following conditions:

temperature 250°C; pressure 2MPa; GHSV 1000

Catalyst	Conversion	CO	n-Alkane proportions		
		(%)	α	C_9-C_{11}	$C_{11}-C_{13}$
10 8. 100 Co:1000 ZSM-5(95)	69	0.68	0.24	0.26	0.29
9. 100 Co:1000 LZ-Y82 ^(a)	47	0.78	0.52	0.56	0.64
10. 100 Co:1000 KW042 ^(b)	80	0.68	0.13	0.18	0.41
11. 100 Co:1000 Bentonite	83	0.72	0.72	0.66	0.60
12. 100 Co:1000 Al_2O_3	66	0.80	0.82	0.80	0.76
(a) commercial faujasite cracking catalyst					
(b) highly dispersed ZSM-5					

20 Example 13

This illustrates the use of dealuminised zeolite Y as a component of the catalyst of the invention. The zeolite Y had a silica/alumina ratio of 8. Conversion was carried out under the following

25 conditions:

Temperature 250°C; pressure 2MPa; GHSV 1000

Catalyst	Conversion	CO	n-Alkane proportions		
		(%)	α	C_9-C_{11}	$C_{11}-C_{13}$
30 13. 100 Co:500HY(8):500 SiO_2	57	0.79	0.60	0.62	0.66

It will be clearly understood that the invention in its general aspects is not limited to the specific details referred to hereinabove.

CLAIMS:

1. Process for the catalytic conversion of synthesis-gas into a product which comprises naphtha (b.p. C₅ to 195°C), kerosine (b.p. 195 to 235°C) and distillate (b.p. 235 to 315°C) characterized in that the catalyst is a Fischer-Tropsch catalyst also containing a zeolite and the naphtha fraction contains 60% or less linear paraffins but the kerosine and distillate fractions contain more linear paraffins and olefins than found in the naphtha fraction.
2. Process according to Claim 1 in which the zeolite has a pore size corresponding to at least 10-ring windows and carries an acidic function.
3. Process according to Claim 1 carried out at a temperature in the range from 220°C to 270°C.
4. Process according to Claim 1 in which the product has a Schulz-Flory alpha value in the range 0.6 to 0.95.
5. Process according to Claim 4 in which the alpha value is in the range 0.65 to 0.85.
6. Process according to claim 1 in which the zeolite is chosen from the group consisting of the ZSM-5 family, ZSM-11, Zeolite Y and dealuminised Zeolite Y.
7. Process according to Claim 1 in which the zeolite is of the ZSM-5 family and the process is carried out under the following conditions:

Temperature	220 to 270°C
Pressure	0.1 MPa to 5 MPa
GHSV	50 to 10,000
Alpha value	0.60 to 0.95

8. Process according to Claim 1 in which the zeolite is of the ZSM-5 family and the process is carried out under the following conditions:

Temperature	220 to 270°C
Pressure	0.1 MPa to 4.0 MPa
GHSV	100 to 5000
Alpha value	0.65 to 0.85

9. Process according to Claim 1 in which the catalyst contains 5 to 50% cobalt and 10 to 90% zeolite, any balance being made up by promoters, inert supports and/or catalyst binders.

10. Process for the catalytic conversion of synthesis gas into a product which comprises naphtha (b.p. C₅ to 195°C), kerosine (b.p. 195 to 235°C) and distillate (b.p. 235 to 315°C) characterised in that the catalyst contains 5 to 50% cobalt and 10 to 90% zeolite of the ZSM-5 family; the process is carried out at a temperature in the range 220 to 270°C, pressure in the range 0.1 MPa to 5 MPa, and GHSV in the range 50 to 10,000; the product has an alpha value of 0.60 to 0.95 and the naphtha fraction of the product contains 60% or less linear paraffins but the kerosine and distillate fractions contain more linear paraffins and olefins than found in the naphtha fraction.

11. A modification of the process according to claim 10 in which the zeolite is chosen from the group consisting of ZSM-11, Zeolite Y and dealuminised Zeolite Y.